

# CATALYSTS FOR DIRECT DECOMPOSITION OF NO<sub>x</sub> IN EXHAUSTS

James H. White, Jeffrey W. Heidrick, Shane E. Roark, and Anthony F. Sammells

jhwwhite@eltronresearch.com

Phone:(303)440-8008

FAX:(303)440-8007

Eltron Research, Inc.

5660 Airport Blvd. #105

Boulder, CO 80301-2340

Joseph D. Wander

Armstrong Laboratory, Environics Directorate

Environmental Risk Reduction Technologies Division

139 Barnes Drive, Suite 2

Tyndall AFB FL 32403-5323

The decomposition of nitrogen oxides in simulated exhaust streams over new brownmillerite catalysts has been investigated at high temperatures and high space velocities. Results are indicative of the occurrence of both reagentless and CO promoted activity in simulated exhaust streams containing up to 16 percent oxygen over the temperature range of 100 - 1000°C. Performance was nonmonotonic in temperature, with an activity maximum occurring between 400 and 500°C. These results suggest the potential efficacy of the catalysts for the direct decomposition of nitrogen oxides in high temperature (400 - 1000°C) exhaust gases, in e.g., gas turbine and diesel engines.

The decomposition of nitrogen oxides under lean conditions absent added reductant is a particularly attractive approach for removal of NO<sub>x</sub> from exhaust streams of diesel engines, lean burn engines, gas turbines, incinerators, and high temperature process streams. Direct decomposition catalysts have been previously reported in the literature.<sup>1-6</sup> Many of these results were obtained under experimental conditions of high NO concentrations(>>1000 ppm) and absent oxygen. Such conditions do not reflect the fact that a few hundred ppm of nitrogen oxides compete with oxygen concentrations of up to 15 volume percent. This three order of magnitude disadvantage renders impractical any catalyst which does not make use (through Lewis acid-base properties) of the relative acid strengths of nitrogen oxides and oxygen.

In addition to acid - base interactions between catalyst and nitrogen oxides, other phenomena must occur. For example, the role of oxygen ion vacancies and their relationship to deNO<sub>x</sub> activity has been clearly demonstrated in the literature.<sup>2,3,6</sup> The adsorbed oxygen anion resulting from dissociation is discharged via oxidation by a transition metal species in the catalyst, followed by combination into molecular oxygen and its subsequent desorption. Reoxidation of transition metal species occurs via desorption of molecular oxygen. Consideration of these requirements has led us to develop new materials based on the brownmillerite structure. The stoichiometries of these materials is such as to provide a high concentration of intrinsic oxygen ion vacancies, while at the same time providing overall material stability.

Catalysts described here have been prepared by the ceramic method and by decomposition of the constituent

metal nitrates on a support (yttria stabilized zirconia - YSZ). Catalysts prepared by either method were calcined at 1000°C for 8 hours. Phase purity was verified by x-ray diffraction. Surface areas of catalysts were obtained by measurement of uptake of nitrogen and application of the Brunauer-Emmett-Teller equation. Temperature programmed desorption (TPD) spectra were obtained using an in-house constructed apparatus. Catalyst activities were measured by passing a simulated exhaust stream over weighed catalyst powder samples heated to the desired temperature with a furnace. The gas stream contained from 475 - 1000 ppm NO in 16 percent O<sub>2</sub>, with helium comprising the balance of the mixture. NO and NO<sub>2</sub> were analyzed by means of electrochemical sensors specific to these respective species. Reaction products (i.e. N<sub>2</sub> and N<sub>2</sub>O) were analyzed by gas chromatography. Reactants and products were also analyzed with a residual gas analyzer (RGA) equipped with a quadrupole mass spectrometer.

X-ray diffractometry for a catalyst designated here as EC-105 and prepared by the ceramic method revealed a dominant phase which has been assigned the brownmillerite structure. A small amount of a second phase was also present, but has not been identified. Nevertheless, the brownmillerite phase appears to be active, since analogs of the material not containing the second phase have comparable or greater activity. The catalyst displayed a TPD spectrum showing a common feature of brownmillerite materials: a steeply ascending portion of the curve at temperatures above 700°C, corresponding to the loss of lattice oxygen. The catalyst also displayed a lower temperature desorption peak, corresponding to the desorption of relatively weakly bound surface oxygen species and suggesting that this catalyst can readily release surface oxygen, freeing sites for NO adsorption.

The catalyst gave an activity maximum at 400°C, almost certainly arising from a competition between the decreasing overall rate of NO uptake with increasing temperature and increasing dissociation rate. At 1000°C, 5.3% conversion of 1000 ppm NO in 16 percent O<sub>2</sub> was obtained at 50,000h<sup>-1</sup>. Incorporation of 1000ppm CO into the gas stream resulted in overall conversion of 34%. Activity of the catalyst was improved by supporting it on yttria-stabilized-zirconia (YSZ). For example, the YSZ -supported catalyst gave 11 percent NO decomposition under the same reagentless conditions. Including CO in the gas stream again increased conversion: at 1000°C and 800,000h<sup>-1</sup> a maximum of 16 percent of the NO was removed from a stream containing 477 ppm NO and 200 ppm CO.

The results presented here show the capacity of these new catalysts to effect NO decomposition under conditions of high temperature and space velocity, conditions appropriate to near combustion environments. Anticipated potential applications are in exhausts of gas turbines, high temperature process heaters, lean burn engines, and diesel engines. In these applications, the catalysts would be expected to be deposited directly onto the walls of combustion chambers or on downstream fixturing. The data obtained thus far point to the possibility of catalyst use in the absence of added reductant.

1. K.Tabata, J. Mat. Sci. Lett., 7, 147(1988).
2. T. Mori, H. Yamamura, H. Ogino, H. Kobayashi, and T. Mitamura, J. Am. Cer. Soc., 77, 2771(1994).
3. S. Shin, Y. Hatakeyama, K. Ogawa, and K. Shimomura, Mat. Res. Bull.,14, 133(1979).
4. Y. Lin and W. K. Hall, J. Phys. Chem., 94, 6145(1990).

5. S. Xie, G. Mestl, M. P. Rosynek, and J. H. Lunsford, J. Am. Chem. Soc., 119, 10186(1997).
6. Z. Zhao, X. Yang, and Y. Wu, Appl. Catal. B: Environmental, 8, 281(1996).